LBL-11661
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

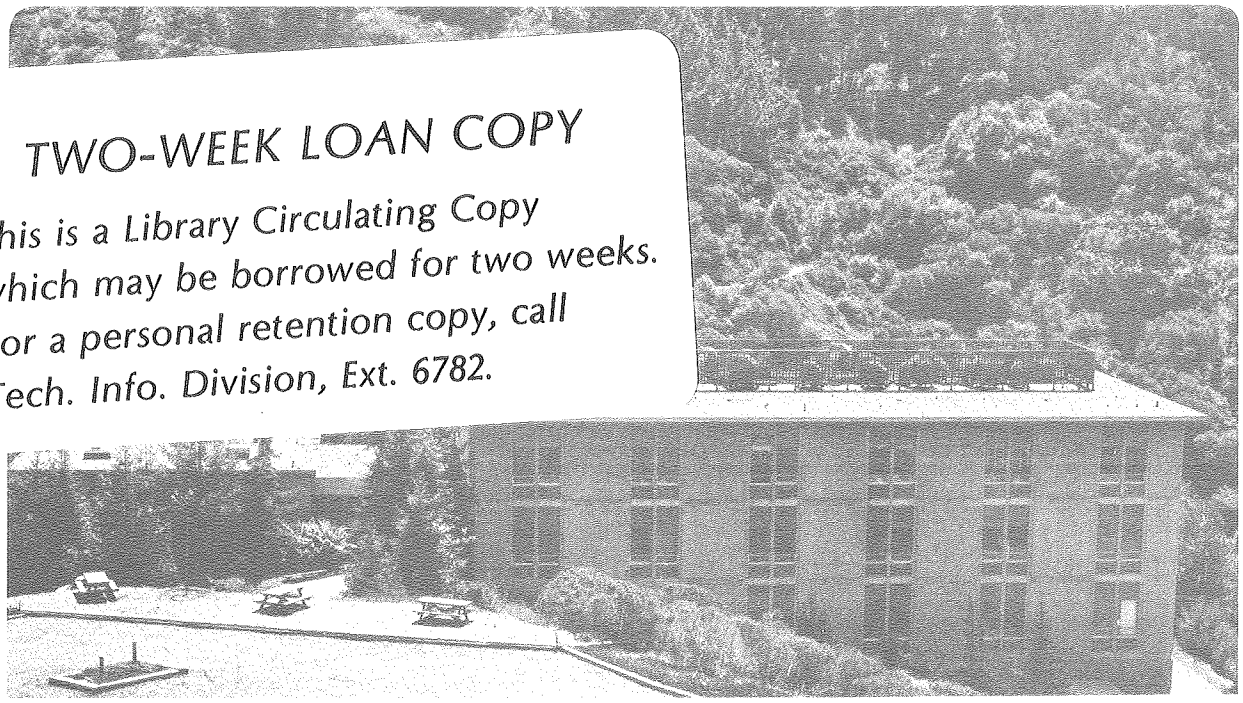
Materials & Molecular
Research Division

Submitted to Physical Review Letters

EVIDENCE FOR PHOTODISSOCIATION OF WATER VAPOR ON REDUCED $SrTiO_3$(111) SURFACES IN A HIGH VACUUM ENVIRONMENT. RELATIONSHIP BETWEEN THE RATE OF HYDROGEN EVOLUTION AND THE SURFACE CONCENTRATION OF Ti^{3+} SPECIES.

S. Ferrer and G. A. Somorjai

August 1980



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

LBL 11661

EVIDENCE FOR PHOTODISSOCIATION OF WATER VAPOR ON REDUCED $SrTiO_3$(111) SURFACES IN A HIGH VACUUM ENVIRONMENT. RELATIONSHIP BETWEEN THE RATE OF HYDROGEN EVOLUTION AND THE SURFACE CONCENTRATION OF Ti^{3+} SPECIES.

S. Ferrer and G.A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, CA 94720, U.S.A.

Abstract

We have observed D_2 photoproduction from D_2O vapor at a pressure of $\sim 1 \times 10^{-7}$ Torr on a reduced $SrTiO_3$(111) crystal face at a temperature of $\sim$600 K. Electron loss spectoscopy data showed a decrease in the surface concentration of Ti^{3+} species while the crystal face was being illuminated and the D_2 photoproduced, indicating that the oxygen was being incorporated into the crystal lattice.

In this letter we report for the first time the photodecomposition of water adsorbed from the gas phase in high vacuum conditions on metal free, reduced $SrTiO_3$ single crystals. In the high vacuum environment we could utilize electron spectroscopies while the reaction was taking place, allowing us to monitor the chemical changes which occurred at the crystal surface. In this way the role of the Ti^{3+} surface species in the photoreaction could be directly established. We have monitored D_2 evolution into the gas phase (by a quadrupole mass spectrometer) from D_2O vapor adsorbed on a reduced $SrTiO_3$(111) crystal face at a temperature of $\sim$600 K. The partial pressure of the water vapor was $\sim 1 \times 10^{-7}$ Torr. Oxygen evolution into the gas phase was not detected and electron loss spectroscopy (ELS) showed a decrease in the surface concentration of Ti^{3+} species while the crystal face was illuminated and D_2 was evolving. From this observation we concluded that the oxygen from the D_2O molecules was being incorporated in the crystal lattice.

Two $SrTiO_3$ single crystals of (111) orientation supplied by National Lead) were used in this study. One was reduced in a hydrogen furnace for several hours at 1000 K resulting in a black colored sample. The other, a transparent sample, received no hydrogen pre-treatment. The UHV system was equipped with a double pass CMA and had UPS, XPS, ELS, LEED, AES, and TDS capabilities (1,2). The base pressure was 1×10^{-10} Torr. The crystal temperatures were measured with chromel-alumel thermocouples in contact with the crystal faces. Band gap radiation was provided by a 500 W mercury lamp. Light from the lamp was focussed and filtered to absorb infrared radiation. Glass cut-off filters were used to select the wavelength range incident on the oxide surfaces. The samples could be irradiated while in front of the electron spectrometer (CMA). The crystals were cleaned by ion sputtering and Auger

spectra were recorded to monitor their cleanliness. ELS spectra were obtained in the second derivative mode using a 100 eV, 1μA primary electron beam. Pt and Ru could be evaporated onto the $SrTiO_3$ crystal faces when desired using a heated tungsten wire as evaporator.

The typical experimental procedure used to observe the water photoreaction was as follows: The clean and reduced $SrTiO_3$ crystal was annealed up to 600-650 K. Then D_2O was leaked into the vacuum system and the pumping speed was reduced by a throttle valve to maintain a steady state flow of D_2O and a partial pressure of D_2O of about $1x10^{-7}$ Torr. Illumination of the crystal surface with photons of energy above the oxide band gap energy (3.2 eV) produced a sudden increase in the D_2 partial pressure that was monitored with the mass spectometer. When the light was turned off, the D_2 partial pressure returned to its initial (dark) value. Figure 1 top curve shows typical mass spectral signals of D_2 when the surface was in the dark or when it was illuminated. The illumination cycles shown in Figure 1 were still reproducible for several hours after starting the experiment. Photoproduction of O_2 or D_2O_2 species were never observed in the mass spectra. Several control experiments were performed in order to ascertain the D_2 photoproduction. We did not observe D_2 photoproduction in the following cases: (a) illuminating the walls of the vacuum system while maintaining the D_2O partial pressure at $1x10^{-7}$ Torr and the crystal hot; (b) keeping the crystal hot and evacuating the D_2O vapor; (c) illuminating the crystal with sub-band gap energy photons; and (d) maintaining the D_2O partial pressure and cooling the crystal to room temperature. When the stoichiometric crystal instead of a reduced sample was illuminated in the presence of $1x10^{-7}$ Torr of D_2O, at 600-650 K, the photoproduction of D_2 did not occur. Deposition

of about 1 monolayer of Pt on the surface of the stoichiometric crystal did not result in D_2 photoproduction either.

We estimated the rate of D_2 photoproduction from the $SrTiO_3$ reduced surface by calibrating the m=4 mass spectrometer signal in terms of D_2 partial pressure and by measuring the pumping speed for D_2 ($\sim$40 ℓs^{-1}). Under conditions of the experiment depicted in Figure 1, the increase on the D_2 partial pressure due to the illumination was $\Delta p \sim 4 \times 10^{-10}$ Torr which corresponds to $\sim 4 \times 10^{11}$ molecules per sec per cm^2. Recently, the photocatalytic decomposition of water vapor at 20 Torr pressure on $NiO-SrTiO_3$ and TiO_2-RuO_2 powder catalysts has been reported (3,4). Although the surface area of the illuminated catalysts were not determined, the H_2 photoproduction rate per sec. and per cm^2 of catalyst can be estimated to be in both cases $10^{11} - 10^{12}$ molecules, which is about the same magnitude that we obtained.

Figure 2 shows a portion of the ELS spectrum of the reduced $SrTiO_3$ surface. The loss peak at 5.6 eV is associated with a bulk transition involving the O2p band and the conduction band. The peak at 1.6 eV is characteristic of surface Ti^{3+} ions and can be used to monitor its concentration (5). The spectra in Figure 2 were obtained during the photoreaction ($\sim$650 K and 1×10^{-7} Torr of D_2O). The spectrum represented by the solid line is from the non-illuminated surface, and the broken line (shifted for clarity) is the spectrum obtained when the crystal surface was being illuminated. The intensity of the 5.6 eV transition does not change upon illumination, but the intensity of the transition at 1.6 eV decreases with respect to its value in the dark. By tuning the CMA to the energy which corresponds to the 1.6 eV transition and plotting its intensity as a function of time in alternating dark - illuminated intervals, the

bottom curve of Figure 1 was obtained which is the mirror image of the top curve. The photoproduction of D_2 (monitored with the mass spectrometer) and the decrease of the Ti^{3+} surface concentration during illumination could be observed to occur simultaneously and were quite parallel; in the control experiments mentioned before (a,b,c, and d) no photoeffect in the Ti^{3+} ELS peak could be observed.

Figure 3 is an Arrhenius plot of the temperature dependence of the D_2 photoproduction rate for a pressure of D_2O of 1.6×10^{-7} Torr. The straight line yields an activation energy of 8.6 kcal mol^{-1}. Studies of the diffusion of oxygen vacancies in $SrTiO_3$ single crystals report an activation energy for bulk diffusion of 6.0 kcal mol^{-1} (6) which is similar to the activation energy for D_2 photoproduction that we found. Therefore, it is likely that the photoreaction is determined by the diffusion controlled availability of oxygen vacancies at the surface of $SrTiO_3$.

The dependence of the D_2 photoproduction rate on the D_2O pressure was also investigated. For a crystal's temperature of 610 K, the photoreaction starts to be detectable at $\sim 2 \times 10^{-8}$ Torr of D_2O. The rate then increases linearly up to $\sim 7 \times 10^{-8}$ Torr and above this value it appears to be pressure independent.

Previous studies have shown the presence of a high concentration of Ti^{3+} species at the reduced $SrTiO_3(111)$ surface (2). Therefore, the surface concentration of oxygen vacancies (V_o) must also be large. We can combine these two facts by formally writing for these defect sites ($2Ti^{3+}$-V_o) to indicate an oxygen vacancy with two bound electrons which are mainly distributed on the positive Ti ions adjacent to the vacant lattice site. According to this scheme we may represent the net photoreaction as

$$D_2O(g) + (2Ti^{3+}\text{-}V_o) + h\nu \longrightarrow D_2(g) + (2Ti^{4+}\text{-}O^{=}_{latt}) \qquad (1)$$

where $h\nu$ stands for the incoming ultraviolet light of larger than band gap energy and $(2Ti^{4+}\text{-}O^{=}_{latt})$ accounts for the incorporation of an oxygen atom into the crystal lattice at the surface which oxidizes the Ti^{3+} ions to Ti^{4+} that are the majority Ti species in the crystal. The mass spectroscopic observation of photoproduced D_2, the lack of detectibility of oxygen evolution, and the observation by ELS that the photodecomposition of D_2O is directly associated with the oxidation of Ti^{3+} ions are all in support of the reaction proposed in Eq.1. The fact that the activation energy of the photoreaction is similar to the activation energy for oxygen vacancy diffusion, suggests that the high temperature is needed primarily to replenish the oxygen vacancies at the surface from the bulk. This model also explains the absence of photoreaction at stiochiometric crystal surfaces where the concentration of oxygen vacancies is much smaller than in the reduced crystals. After a long series of experiments, the reduced $SrTiO_3$ crystal, initially quite opaque, started to be more transparent, indicating net oxidation.

It should be noted that the observed photoreaction is stoichiometric. Attempts to make it catalytic (which was observed at higher partial pressures of water vapor (3,4) and in the presence of sodium hydroxide (7)) were unsuccessful. Deposition of one monolayer of Pt or Ru on the surface of the reduced $SrTiO_3$ crystal did not cause any detectable oxygen evolution. The correlation between this stoichiometric reaction observed at low pressures on reduced $SrTiO_3$ surfaces and the catalyzed photoreaction at high pressures, which leads to the evolution of both hydrogen and oxygen molecules, will have to be determined in the near future.

Based on previously published studies of $SrTiO_3$ and TiO_2, we would

like to propose a model for the intermediate steps that lead to Eq.1.

$$2D_2O(g) \xrightarrow{Ti^{3+}\ rich} 2DO^- + 2D^+ \quad (2)$$

$$2h\nu \longrightarrow 2\ e^- + 2h^+ \quad (3)$$

$$2h^+ + 2DO^- \longrightarrow 2DO \longrightarrow D_2O_2 \longrightarrow D_2O+O \quad (4)$$

$$(2Ti^{3+} - V_o) + O \longrightarrow (2Ti^{4+} - O^{=}_{latt}) \quad (5)$$

$$2e^- + 2D^+ \longrightarrow 2D \longrightarrow D_2(g) \quad (6)$$

Where: Eq.2 shows that water dissociates upon adsorption in the dark on a reduced surface (1,2); Eq.3 represents the electron-hole pair formation in the conduction and valence bands, respectively, upon illumination; Eq.4 is the hole capture by the basic hydroxyl species (8) leading to the formation of deuterium peroxide which decomposes to water and oxygen; Eq.5 represents the incorporation of an oxygen atom to an oxygen surface vacancy resulting in an oxidation of the Ti^{3+} ions; and Eq.7 represents the reduction of deuterium ions to atomic deuterium which recombine to form a D_2 molecule that leaves the crystal surface.

This work was supported by the Chemical Sciences Division of The U. S. Department of Energy under Contract W-7405-ENG-48.

References

1. W.J. Lo, Y.W. Chung, and G.A. Somorjai, Surf. Sci. 71, 199 (1978).

2. S. Ferrer and G.A. Somorjai, Surf. Sci. 94, 41 (1980).

3. K. Domen, S. Naito, M. Soma, T. Onishi, and K. Tamaru, J.C.S. Chem. Comm. 543, 1980.

4. T. Kawai and T. Sakata, Chem. Phys. Lett. 72, 87 (1980).

5. V.E. Henrich, G. Dresselhaus, and H.J. Zeiger, Phys. Rev. Lett. 36, 1335 (1976).

6. L.C. Walters and R.E. Grace, J.Phys. Chem. Sol. 28, 245 (1966).

7. F.T. Wagner and G.A. Somorjai, Jour. Am. Chem. Soc. 102, 5494 (1980).

8. G. Munuera, V. Rives-Arnau, and A. Saucedo, Jour. Chem. Soc. Farad. Trans I 75, 736 (1979).

Figure Captions

Fig.1 Top curve - intensity of the m=4 signal as a function of time for several dark-illumination cycles. Bottom curve - intensity of the Ti^{3+} ELS signal as a function of time for the same dark-illumination cycles.

Fig.2 Solid line - ELS spectrum of the reduced $SrTiO_3$(111) surface at the photoreaction conditions in the dark. Broken line - (shifted for clarity) the same, but while illuminating the crystal face. The elastic peak is shown for reference.

Fig.3 Arrhenius plot of the D_2 photoproduction rate.

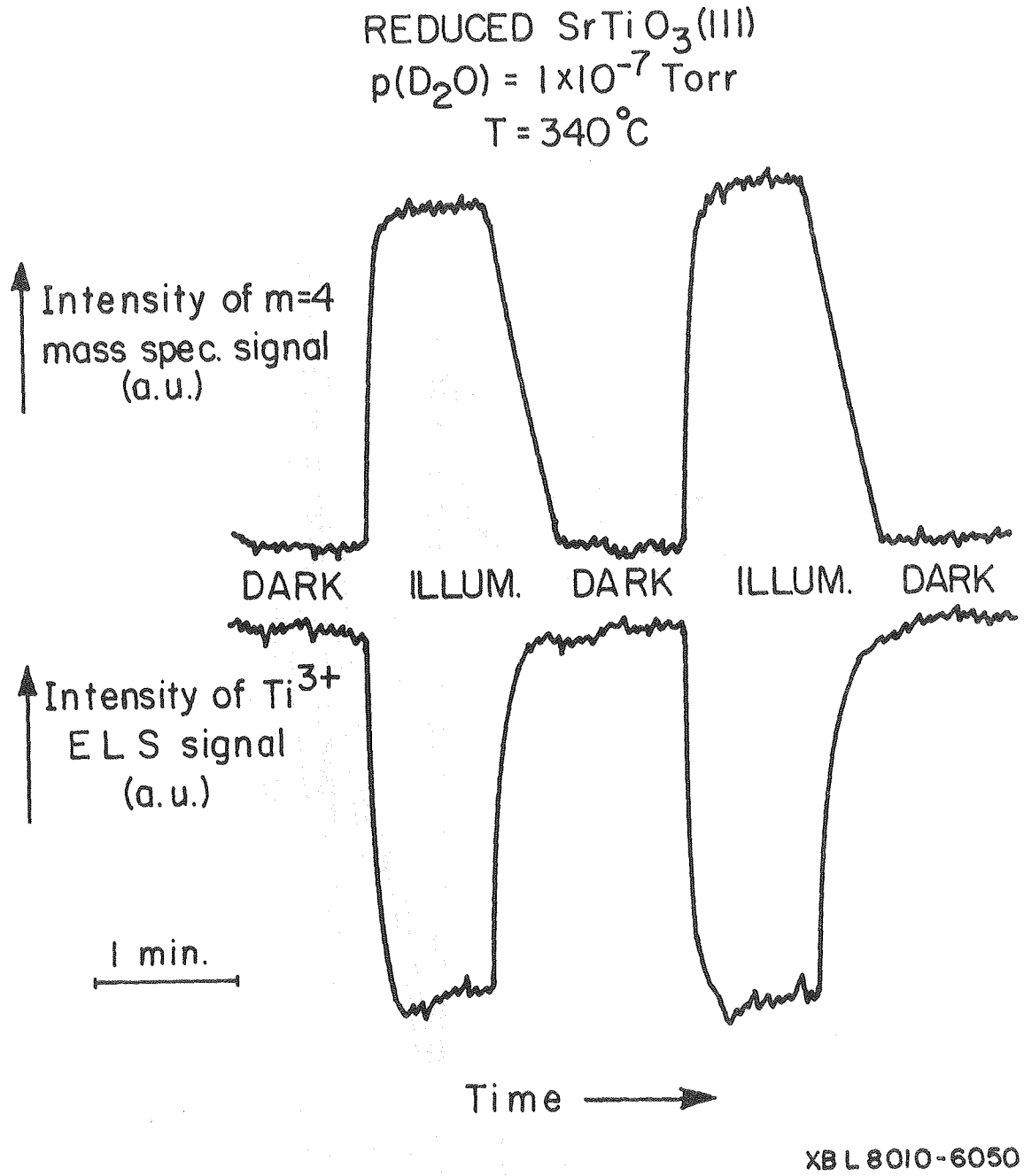


Fig.1

Ferrer et al.
Fig 1

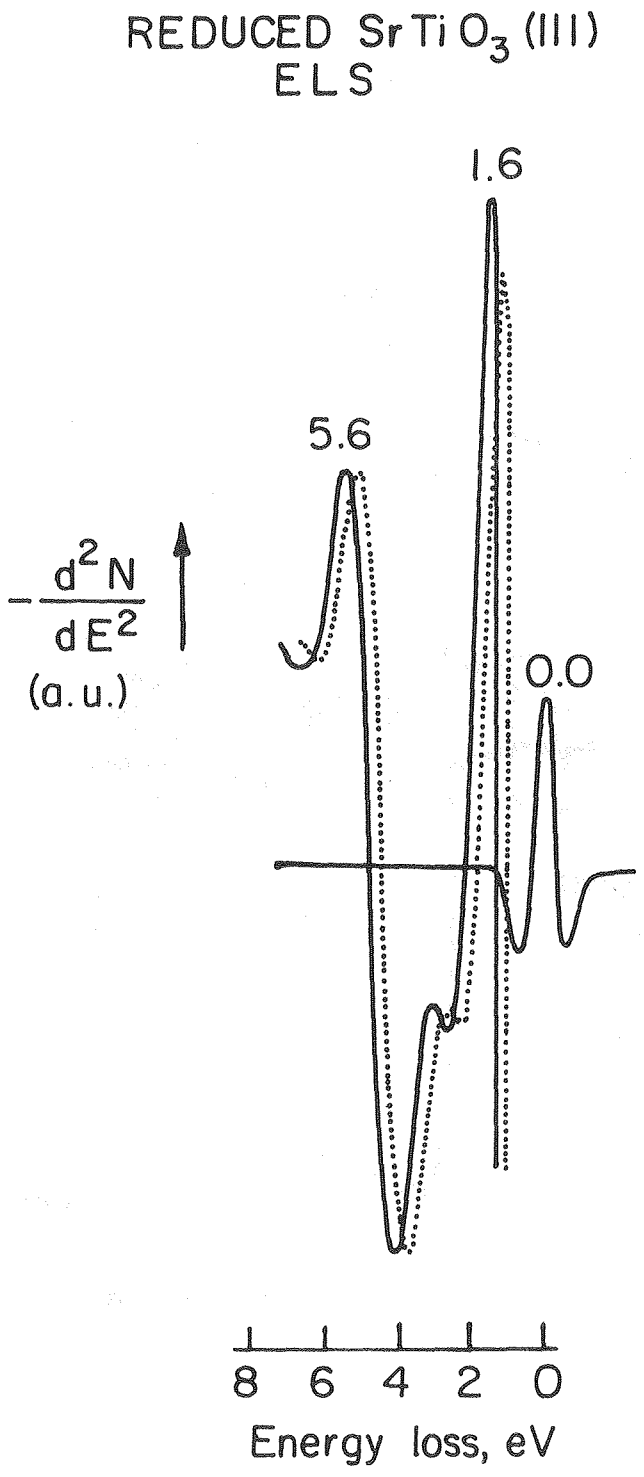
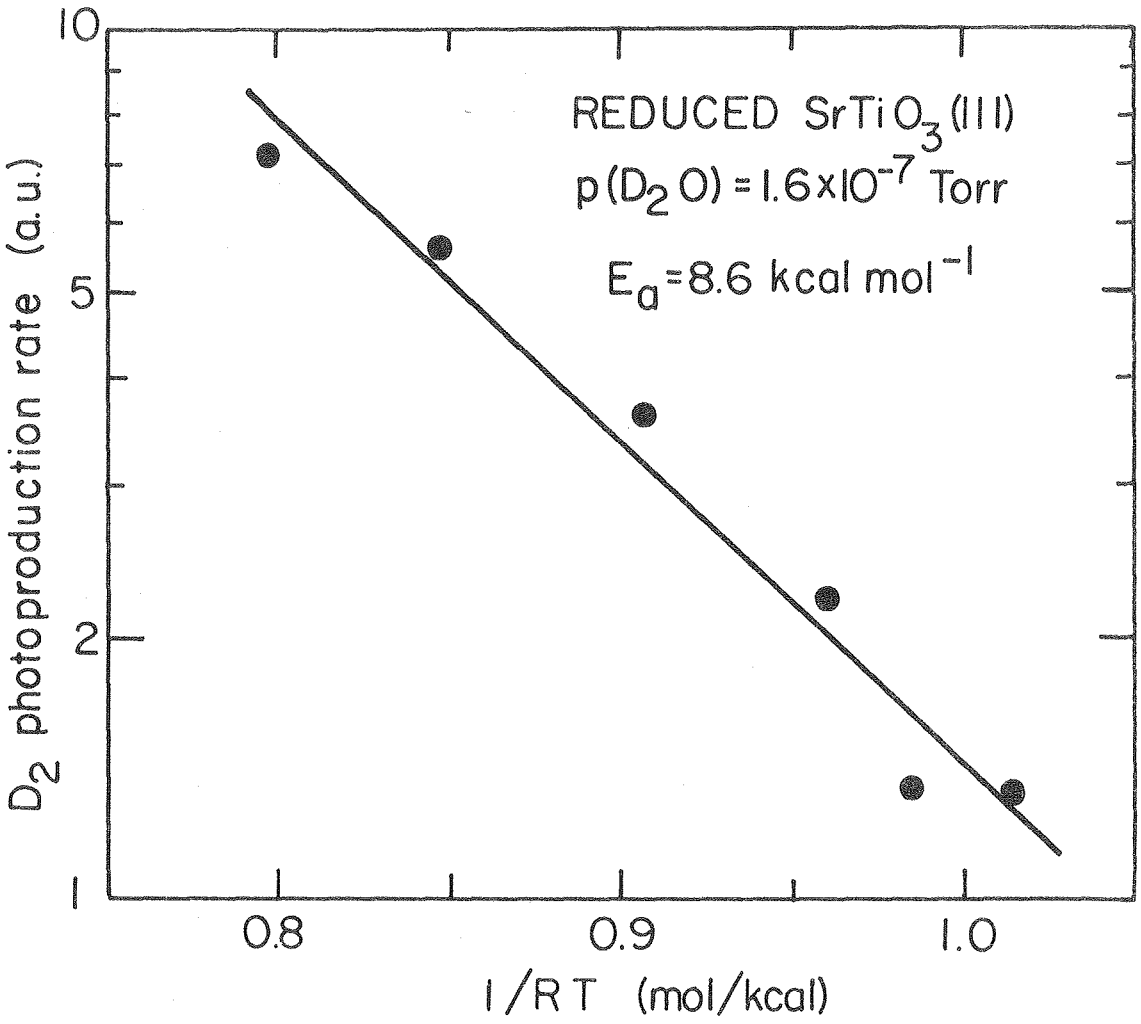


Fig.2

Ferrer et al.
Fig 2



XBL 8010-6049

Fig.3

Ferrer et al.

Fig. 3